

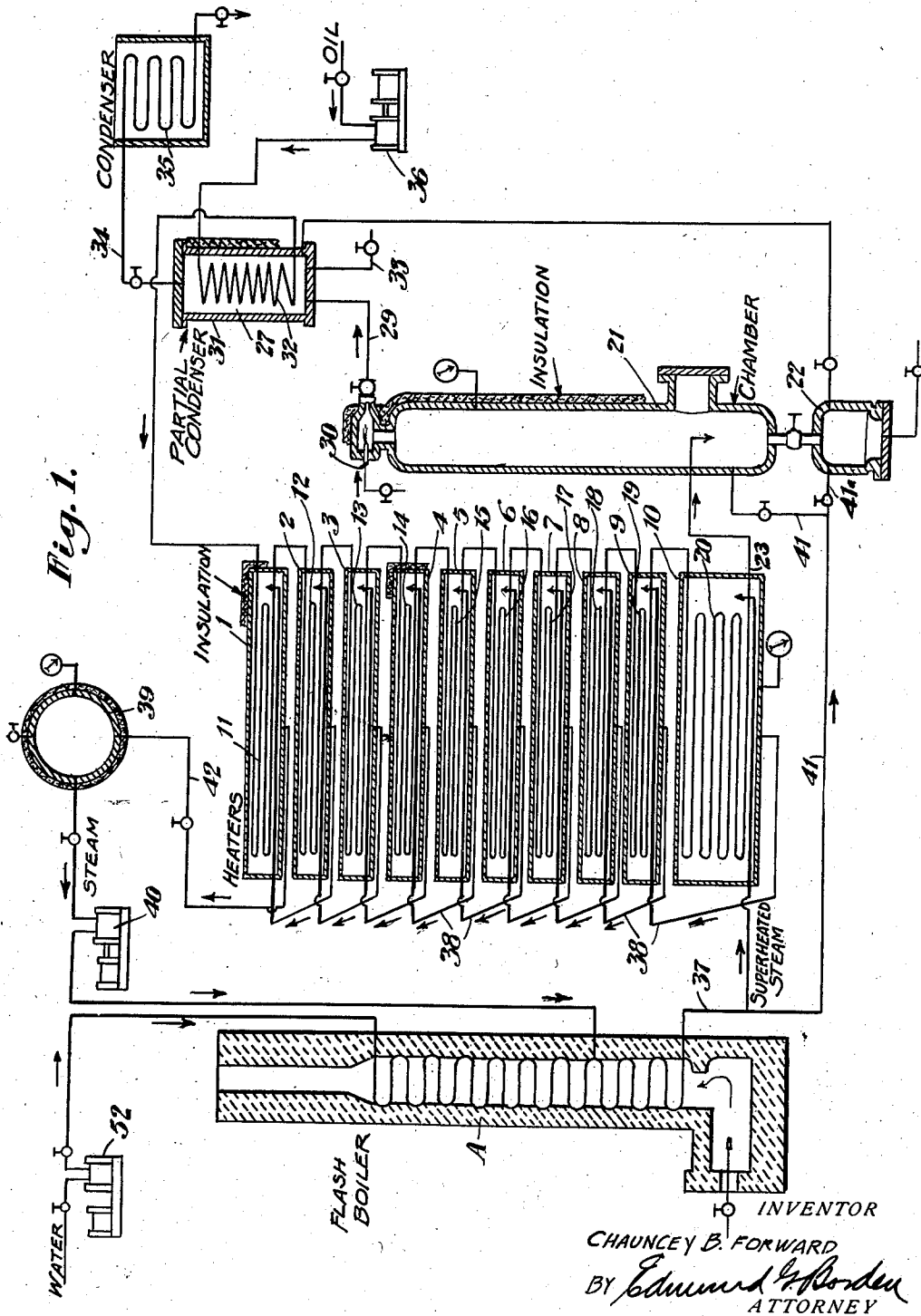
June 21, 1938.

C. B. FORWARD

2,121,027

PROCESS FOR CRACKING HYDROCARBONS

Original Filed Nov. 23, 1927 2 Sheets-Sheet 1



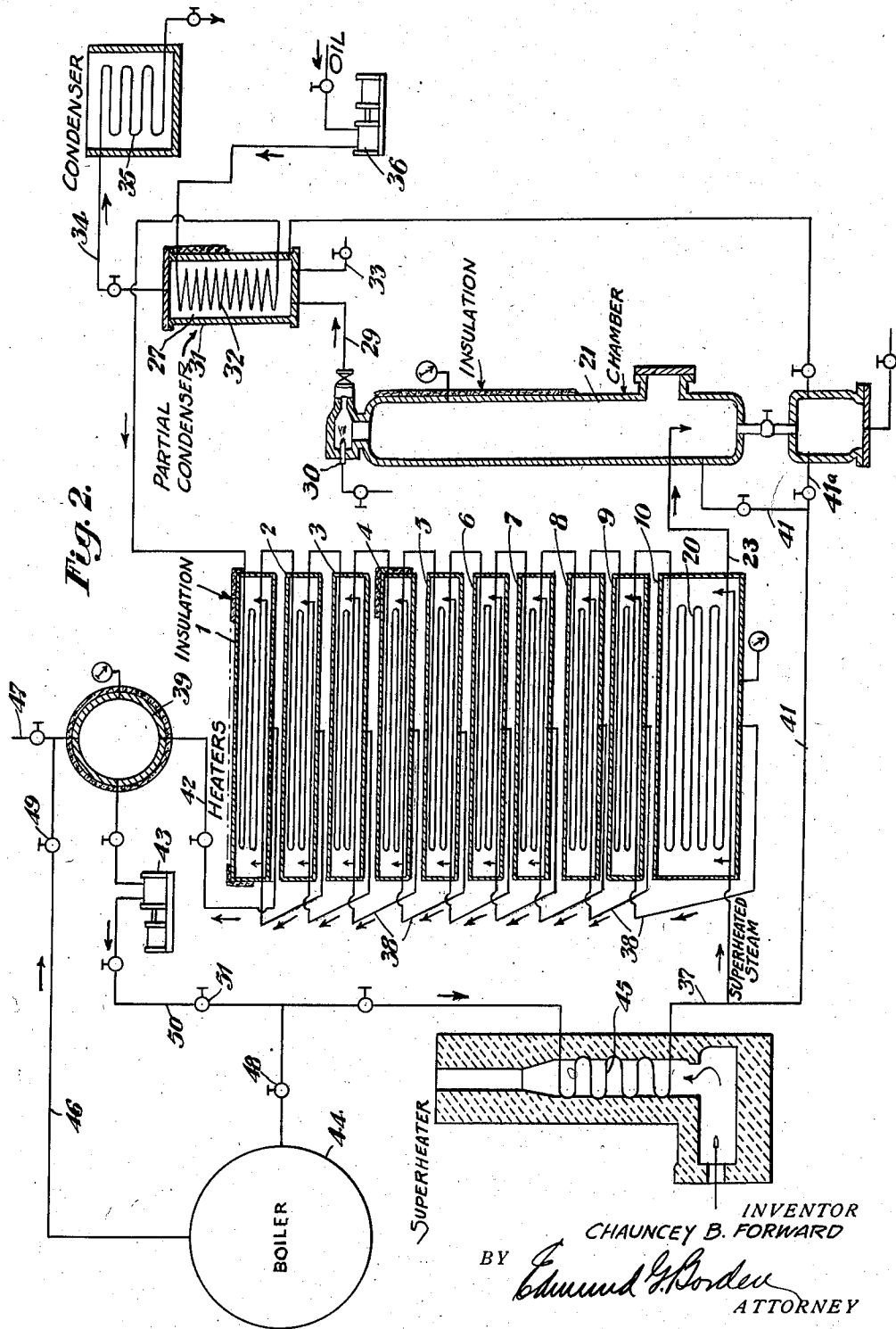
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UNITED STATES PATENT OFFICE

2,121,027

PROCESS FOR CRACKING HYDROCARBONS

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Original application November 23, 1927, Serial No.
235,206. Divided and this application April 3,
1933, Serial No. 664,082

8 Claims. (Cl. 196—61)

This invention relates to improvements in the art of cracking hydrocarbon oils for the production of more desirable hydrocarbon compounds of both lower and higher boiling point ranges. The invention comprises an improved process which is of especial value and application in the production of distillates suitable for use as motor fuels in internal combustion engines, from petroleum oils and fractions thereof. The invention includes an improved process and an improved hydrocarbon product. This application is a division of my co-pending application Serial No. 235,206, filed November 23rd, 1927, for Art of cracking hydrocarbons which is in turn a continuation in part of my co-pending applications Serial Nos. 318,484; 665,537 and 682,477 filed August 19, 1919, September 29th, 1923 and December 24, 1923, respectively.

It has been known that cracked distillates obtained by cracking special fractions derived from certain naphthene and asphalt base crude oils have to a limited extent the ability to inhibit detonation of slightly higher pressures than those encountered in internal combustion engines of the present day automobile. It is also known that in exceptionally high temperature cracking operations such as those carried out in connection with the manufacture of gas for illuminating purposes, a low percentage of the stock charged may be obtained as a by-product distillate or condensate having good detonation inhibiting characteristics, but such distillates or condensates have the disadvantage of ordinarily containing a relatively high percentage of unsaturated compounds which decompose readily with the formation of gum which it is practically impossible to remove without excessive loss of the more stable unsaturated compounds. Such distillates also have a very offensive odor. Further, the major portion of the charging stock is converted into a permanent gas and only a relatively small yield of a condensate boiling within the range of present day internal combustion engine motor fuel specifications is obtained from cracking operations of this variety. The reactions incident to such operations are also accompanied by excessive formation of coke and carbon-like materials.

It has been universally assumed by petroleum refiners, petroleum chemists and even organic chemists as a group, that vapor phase cracking of petroleum hydrocarbons at high temperature is invariably accompanied by the formation of coke. This assumption has apparently been corroborated by the fact that all of the very high

temperature vapor phase cracking processes heretofore developed, so far as I am aware, have been accompanied by excessive coke formation and the difficulties incident to this formation of coke and carbon-like materials have constituted a serious engineering problem and frequently resulted in disaster. I have discovered that this coke formation is unnecessary in the vapor phase cracking of petroleum oils even when very high temperatures are employed, and further that by vapor phase cracking at high temperature so conducted as to avoid coke formation, a distillate product is produced which is chemically quite different from the distillate products of ordinary cracking processes and which has desirable physical characteristics superior to any product now known.

Distillate products produced by the improved process of the invention are characterized by their high critical compression when used as motor fuels in internal combustion engines; their ability to increase the critical compression of other petroleum distillates with which they may be blended; their high specific gravity relative to the specific gravity of ordinary petroleum distillates having a corresponding range of boiling points, their stability and relative freedom from gum-forming constituents in their crude state and without further treatment and their superior ability to develop power when used as motor fuels in internal combustion engines, especially in engines having a high compression ratio.

The process of the invention is adapted to produce a distillate product having a high critical compression from even the most refractory petroleum oils and distillates, including pure paraffine base oils from which the distillates obtained by ordinary cracking processes are notable for their detonation characteristics even at low pressures, with conversion of only a comparatively small percentage of the charging stock into fixed gas and with substantially no coke formation. For example, I have produced from a purely paraffine base gas oil by the improved process of the invention, a large yield of a distillate product that would operate successfully as a motor fuel in an internal combustion engine having a compression ratio greater than 11 to 1, without audible detonation under conditions other than compression ratio, at which it was impossible to operate without audible detonation with a compression ratio greater than 4.3 to 1, when using a straight run Pennsylvania gasoline as the motor fuel and at which it was impossible to operate without audible detonation with a

compression ratio greater than 5.43 to 1 when using a blend of 50% pure benzol and 50% straight run Pennsylvania gasoline as the motor fuel. Further, when using samples of the improved distillate product as the motor fuel, the engine operated satisfactorily, though with regular detonation, when the compression ratio was increased to greater than 14 to 1.

According to the process of the invention, an advancing stream of the oil, preferably a gas oil or heavy naphtha distillate, is heated, vaporized and the generated vapors superheated to a temperature substantially in excess of their boiling point at the pressure employed so that the major part of the cracking reaction takes place in the vapor phase. The superheated oil vapors are then subjected to a digesting operation for a considerable period of time at a uniform and accurately controlled temperature during which heat is supplied to the vapors at substantially the rate at which heat is absorbed in the reactions taking place. The stream of oil or vapors during the heating operation and during the digesting treatment above referred to is maintained in motion at a relatively high velocity and is heated by heat transfer from a heating medium positively circulated preferably countercurrent to the flow of oil and vapors and in indirect contact heat exchanging relation therewith. I find it advantageous to employ a gaseous heating medium so that all difficulties incident to solidification and the necessity of supplying latent heat of vaporization are avoided over the temperature range employed and a more even distribution of the heating effect obtained. When employing a gaseous heating medium a relatively high velocity of flow over the heating surfaces should be maintained. The temperature of the heating medium is maintained only slightly higher than that of the oil or vapors being heated or undergoing the cracking reaction so that a uniform heating effect is obtained. The cracked vapors may advantageously be subjected to a further digesting treatment in an enlarged heat insulated zone during which no heat is supplied from an external source and the vapors are maintained above their cracking temperature by their self-contained heat. An additional amount of conversion may take place during the last named digesting operation.

The cracked vapors from the digesting operation are preferably chilled suddenly from at or above the cracking temperature to below the cracking temperature, for example, by injecting a cooling medium, such as water or a relatively cool liquid hydrocarbon into the vapor stream at the point of discharge from the digesting zone. The injection of a cooling liquid into the vapors discharged from the digesting operation before their temperature has been materially reduced serves to prevent the formation of coke incrustations in any subsequent part of the system in such a manner as to foul the apparatus. Water may advantageously be employed as the cooling medium because of its high latent heat.

The entire charge of cracked vapors may be condensed to form a single overhead distillate and any desired fraction separated therefrom by subsequent redistillation, or the vapor stream may be chilled from at or above the cracking temperature to below the cracking temperature, but not to below the condensing point of the major portion of the cracked vapors, and the vapors remaining uncondensed subsequently fractionally condensed in a suitable dephlegmator to secure

any desired end boiling point distillate without redistillation. The fresh oil supplied to the stream may be preheated by heat exchange with the hot vapors and the cooling action of the fresh oil utilized to effect partial condensation of the vapors. The pressure maintained on the vapors during the cracking treatment will vary with the character of the product desired and the character of the oil used as charging stock. For example, the digesting operation may be carried out under substantially atmospheric pressure and the oil supplied to the heating coils at the pressure necessary to maintain the desired rate of flow therethrough. Or, a pressure in excess of 250 pounds per square inch may be maintained on the vapors in the enlarged digesting zone and the oil supplied to the heating coil at a pressure of from about 400 to 600 pounds per square inch or higher. In general, the higher the pressure employed the greater will be the yield and the higher the quality of hydrocarbon constituents obtained which are of value as detonation inhibitors.

The process of the invention will be further described in connection with the accompanying drawings which illustrate in a diagrammatic and conventional manner one form of apparatus adapted to carry out the process of the invention, but it is intended and will be understood that this further description and illustration are for the purpose of exemplification and that the invention is not limited thereto.

Fig. 1 is a conventional representation in elevation and partly in section of one form of apparatus adapted to carry out the process of the invention.

Fig. 2 is a diagrammatic representation in elevation of a modification of the type of apparatus illustrated in Fig. 1.

Referring to Fig. 1 of the drawings, A is a boiler and superheater similar to that described and illustrated in my former application Serial No. 318,484 to which reference has previously been made. The drums 1 to 9 are provided with coils 11 to 19, respectively, of relatively small pipe which are connected in series to form one long continuous coil. The size and length of the coils may of course be varied. In one installation in which the drums 1 to 9 were about 12 inches in diameter and 18 feet long, the coils were built of $\frac{3}{4}$ inch pipe and were each approximately 500 to 600 feet in length. The drum 10 is provided with the cracking or digesting coil 20. This coil may advantageously be considerably longer than any one of the coils 11 to 19 and is connected to form a continuation of the latter and to discharge into the digesting chamber 21. For example, in the installation above referred to the drum 10 was about 18 feet long and 24 inches in diameter and the coil 20, constructed of 1 inch pipe, approximately 2300 feet in length. The latter portion of the continuous coil formed by the units 11 to 20 may advantageously be of a slightly greater diameter than the initial portion to decrease the resistance to flow due to expansion of the generated vapors. The drums 10 to 1 are connected in series by connections 38 arranged to convey the highly heated gaseous heating medium successively therethrough and are heavily heat insulated to prevent loss of heat by radiation. Connection 37 is arranged to convey superheated steam from the superheater A to the drum 10. Branch connections 41 and 41a are provided to permit superheated steam to be supplied directly to the chamber 21 and auxiliary chamber 75

22, when desired, for example, during preliminary heating of the apparatus.

In the installation above referred to, the chamber 21 consists of a vertical drum approximately 3 feet in diameter and 23 feet in length. This chamber is preferably heavily heat insulated, though if desired loss of heat therefrom by radiation may be prevented by circulating heating gases of the same or slightly higher temperature than the oil vapors thereover.

Chamber 21 is shown in communication with heat exchanger 27 through valved connection 29. A jet 30 in the connection 29 adjacent chamber 21 is arranged to permit a cooling fluid, such as water, to be injected in regulated amounts into the stream of vapors as they are discharged from the chamber 21. The heat exchanger illustrated comprises a shell 31, having a coil 32 arranged therein. A draw off connection 33 leads from the lower part of the heat exchanger. A vapor connection 34 leads from the top of the heat exchanger to the water cooled condenser 35. The fresh oil pump 36 is connected to the upper end of the coil 32 and the lower end of the coil is connected to one end of the heating coil 11 in the drum or jacket 1. The heating medium, for example superheated steam, is conveyed from the heater A while at its maximum temperature through connection 37 to drum 10, where it circulates rapidly over the coil of pipe therein, and then passes consecutively through drums 9 to 1 from whence it is conveyed at a reduced temperature through connection 42 to steam receiver 39. The pressure in the steam receiver 39 is maintained a sufficient amount lower than the pressure in the heater A to insure a rapid flow of the heating medium over the heating coils.

Steam withdrawn from the receiver 39 at a reduced temperature may be reheated and again employed as a heating medium in another similar apparatus, or returned to the original heater and recycled through the same system, or it may be employed as industrial steam for any other purpose desired. Compressor 40 is arranged to withdraw steam from the receiver 39 and increase the pressure on the steam so withdrawn an amount sufficient to overcome the frictional resistance to flow through the system, when it is desired to recycle the steam through the original system.

Reheating the steam has the advantage of requiring only superheat to raise the temperature of the steam to any desired point, thereby avoiding the necessity of supplying latent heat.

I find it advantageous to maintain a relatively high pressure on a gaseous heating medium so as to increase the effectiveness of the heat transmitting surfaces, through which heat is transmitted to the oil or vapors. In this connection I have found steam to be a particularly advantageous heating medium because of its high specific heat and the convenience of securing large amounts under a high pressure and at a high temperature. Where steam is to be the heating medium and an arrangement of generator and superheater, in which an advancing stream of water is vaporized and superheated while passing through a single continuous coil is employed, as illustrated in Fig. 1, the compressor 40 may advantageously be arranged to introduce the compressed steam into the boiler A at approximately the point at which vaporization of the stream of water supplied by the pump 52 is substantially complete.

Where it is desired to employ a superheater independent of the boiler, as in the arrangement

illustrated in Fig. 2, the compressor 43 may be arranged to discharge steam withdrawn from receiver 39 through line 50 containing check valve 51 directly into the line communicating between the boiler 44 and the superheater 45. In order to secure accurate control, the arrangement of apparatus illustrated in Fig. 2 may with advantage be operated so that the entire quantity of steam passing through the superheater 45 and drums 10 to 1 is supplied directly from the receiver 39 by the compressor 43, and such additional steam as is necessary to compensate for any slight losses throughout the system supplied directly to the drum 39 from the boiler 44 through connection 46. When operating in this manner the valve 48 is closed and the valve 49 opened.

An arrangement of apparatus similar to that just described is also advantageous where a gaseous heating medium other than steam, for example nitrogen, carbon dioxide, or other gaseous substances, preferably inert to reduce fire hazard, is employed. When so operating, circulation of the heating medium may be maintained entirely by the compressor 43, and such additional gaseous substances as are required to compensate for leakage from the system introduced directly to the receiver 39 from any suitable source of supply, for example through connection 47.

In the operation of the apparatus illustrated in Fig. 1, fresh oil supplied by the pump 36 is forced through coil 32 in heat exchanger 31, where it is initially heated by the hot cracked vapors, to the inlet of coil 11 and passed serially through coils 11 to 20 in countercurrent flow and in indirect contact heat exchanging relation with the superheated steam circulating through drums 10 to 1 successively. During the passage of the oil through coils 11 to 19, the temperature of the oil is raised to approximately 900 to 1000 degrees F. below which temperature vaporization of substantially the entire charge occurs. This heating is effected gradually by heat transfer with steam the temperature of which is only slightly higher than that of the oil being heated. The hot oil vapors from coil 19 enter the coil 20 at a temperature only slightly below the temperature of the steam in the drum 10. While the highly heated oil vapors are traveling through the coil 20 in a stream of restricted cross section they are maintained at a high temperature for a prolonged period of time. Since no vapors are withdrawn at an intermediate point in the coil 20 and the flow of vapors therethrough is maintained at a high velocity, substantially no segregation of the heavier and lighter constituents is permitted. The hot cracked vapors discharged into the heat insulated digesting chamber 21 through connection 23 may continue to undergo a cracking reaction and as their velocity is materially reduced in the digesting chamber any small amount of free carbon that may be released from the vapors may be permitted to settle to the bottom of the digesting chamber in the form of a light finely divided dry powder resembling carbon black. This carbon which is negligible in amount and ordinarily will not exceed 1.0% of the total oil charged may be blown off from time to time to the auxiliary chamber 22, without interrupting the cracking operation, when it is desirable to collect it separately. If it is not desirable to separately collect this negligibly small amount of free carbon, the finely divided powder may be carried on through the system with the vapor stream, for example, by arranging the discharge end of con-

nection 23 sufficiently close to the lower end of chamber 21 so that the blast of vapors will prevent settling.

The temperature of the cracked vapors in the chamber 21 to be most advantageously employed will vary from about 875 to 1050 degrees F. depending on the kind of oil being treated and the character of the distillate it is desired to obtain. The vapors escaping from chamber 21 are suddenly chilled to below their cracking temperature by injecting water or other suitable cooling fluid into the vapor stream at the point of discharge from the digesting chamber and before the temperature of the vapors has been materially reduced below the temperature at which they were maintained in the digesting chamber. The injection of a sufficient quantity of water to reduce the temperature of the oil vapors to about 700 degrees F. has been found in practice to satisfactorily prevent the formation of carbon incrustations in any part of the apparatus through which the vapors or condensate thereof are subsequently required to pass. The vapors leaving the chamber 21, and subsequent to the chilling operation above referred to, may be advantageously passed through the heat exchanger 27 in heat exchanging relation with the fresh oil supplied to the system through the coil 32 to recover a portion of the heat contained therein. When the apparatus illustrated is so operated the vapors will be subjected to a refluxing action by the cooling effect of the fresh oil and the condensate so formed may be drawn off through connection 33. Vapors escaping uncondensed from the heat exchanger may be passed directly to the water cooled condenser 35 and condensed therein to form a single overhead distillate, which may be fractionally redistilled as desired, or the vapors escaping from the heat exchanger may be fractionally condensed in a suitable fractional condenser to secure products of the desired boiling point range directly.

The uncondensed vapors and gases escaping from the final condenser may be treated by absorption or compression for the recovery of readily condensable constituents contained therein. These gases furthermore are particularly rich in constituents suitable for the production of alcohols and other organic derivatives or substitution products.

Due apparently to the gradual heating of the oil and vapors in the coils 11 to 19 and the prolonged exposure of the oil vapors to high temperature in the coil 20, the discharge temperature of the oil vapors from the latter is very critical and substantial variations in the temperature at this point, as well as in the pressure and the rate of throughput, will cause a marked variation in the character, not only of the composite distillate product obtained, but also in the character of fractions having similar boiling point ranges. The character of the distillate is also materially affected by the length of the time of exposure to high temperature as governed by the length of the coil 20. The exact temperatures, pressures and rate of throughput to be most advantageously employed in a given apparatus will, of course, vary with the character of the distillate product it is desired to obtain, as well as with the character of the initial charging stock. The effects of variation in the temperature employed and in the time of exposure of the oil to high temperatures as governed by variations in the length of the coil 20 may be

best illustrated by specific examples of runs made under different operating conditions.

I do not know the exact chemical composition of certain components of the distillate products that may be produced by the improved process of the invention, but some of their physical characteristics differ radically from all other natural or cracked petroleum distillates of a similar range of boiling points of which I am aware. For example, I am not certain that all of the constituents referred to as aromatic hydrocarbons are true members of the aromatic series and in referring to aromatic hydrocarbons, naphthenes and unsaturated hydrocarbons in the description of the distillates or fractions thereof when operating under different conditions, as hereinafter described, and in defining the distillate products in the claims appended hereto, I refer to such constituents as react similar to aromatic hydrocarbons, naphthenes and unsaturated hydrocarbons when a distillate containing them is subjected to the following tests developed by Dr. J. R. Withrow, professor of chemical engineering, Ohio State University, Columbus, Ohio, and hereinafter described.

Unsaturated hydrocarbons

A 100 cc. charge of the product to be tested is distilled in a 100 cc. Engler (A. S. T. M.) distilling flask, using the standard Government and A. S. T. M. equipment as used in the distillation test for gasoline. This distillation is stopped immediately upon the appearance of cloud in the distilling flask and the temperature at which cloud appears noted. The residue in the flask is discarded. The distillate obtained in the above operation is treated with 80% sulphuric acid, in the volume ratio of acid to oil of 2:1. The mixture is agitated for fifteen minutes and then allowed to settle at least twelve hours. The volume of the oil layer formed on settling is measured and the percent decrease of this volume is calculated on the basis of the distilled fraction. This calculation gives the percentage of unsaturated hydrocarbons that have dissolved in the acid layer as reaction products.

The acid treated oil is washed with water, neutralized with a 10% solution of sodium hydroxide allowed to settle in a separatory funnel, the aqueous layer drawn off and the oily layer then redistilled in the distillation apparatus above described, and to the temperature above noted. The volume of the residue of the second distillation is measured and is calculated as a percentage of the first distillation fraction. This represents the percentage of the unsaturated hydrocarbons that have been polymerized during the acid treatment. This value, added to the percentage of unsaturated hydrocarbons dissolved by the sulphuric acid, gives the total percentage of unsaturated hydrocarbons in the original distillation fraction.

Aromatic hydrocarbons

Into a 100 cc. burette provided with a glass water bath are put 20 cc. of the second distillation fraction (freed from unsaturated bodies) and 50 cc. of nitrating mixture added slowly with mixing (by tilting tube) and cooling (passing cold water through water jacket). The nitrating mixture consists of nitric acid 25%, sulphuric acid 58% and water 17%. This operation should require from 15 to 60 minutes and great care must be taken to avoid heating, which may cause side reactions and possible explosion, and errors in

reading due to double nitration. The reaction mixture is allowed to stand until the evolution of gas ceases. The nitrated bodies form a layer between the spent acid and the residual oil. The number of cc. of nitrated bodies is read off from this layer and this value multiplied by the factor 4.3 will give the percentage of aromatic hydrocarbons in the second distillation fraction. From this the percentage in the first distillation fraction can be readily calculated.

Naphthenes

The oil from the nitration treatment is washed with water and a 10% solution of sodium hydroxide and subsequently thoroughly dried with calcium chloride. The aniline value is determined on this dried oil, which is a mixture of paraffine and naphthene hydrocarbons. Ten cc. of freshly distilled aniline and an equal volume of the oil are placed in a test tube that is jacketed by a larger test tube. Into the smaller test tube are placed a thermometer (calibrated in 0.1 degree C.) and a stirring rod. The mixture is heated until the cloud disappears and the temperature at this point is read. The heating is continued until the solution is just above the cloud point and then allowed to cool until the cloudiness reappears. This cloud point is read to 0.1 degree C. Under the conditions of the test, the paraffine hydrocarbons are completely miscible with aniline at 70 degrees C., and the cloud point is depressed 0.3 degree C. for each 1% of naphthene hydrocarbons present. The difference between the temperature at the cloud point and 70 degrees C. divided by 0.3 will give the percentage of naphthene hydrocarbons in the oil from the nitration treatment. This percentage may then be calculated back to the original distillation fraction to find the percentage of naphthene in the original fraction.

Paraffines

The percentage of paraffine hydrocarbons in the original distillation fraction is obtained by subtracting the sum of the percentage of unsaturated, aromatic and naphthene hydrocarbons from 100.

In order to determine the detonation inhibiting characteristics of the distillates obtained by various methods of operation, the distillates themselves and various fractions and blends of the distillates with straight run paraffine base gasoline were tested as motor fuels in an internal combustion engine, and the results obtained thereby, compared with tests made in the same engine under similar conditions using a gasoline obtained by straight distillation from a Pennsylvania crude oil, and blends of this gasoline with pure benzol boiling substantially entirely within a range of 1 degree C. The straight run Pennsylvania distillate employed in making these tests was a distillate having an initial boiling point of 137 degrees F. and an end boiling point representing 96% over at 406 degrees F.

The engine used in making these tests was a 3 x 4 single cylinder, water cooled, four cycle engine of the valve in head type. All tests were made with a fixed spark advance of 20 degrees and an engine speed of 1080 revolutions per minute. The torque of the engine was measured by a cradled generator. The engine was so constructed that the compression ratio could be varied over a considerable range while the engine was operating, without material change in the valve timing or lift. The compression ratio at which detona-

tion was first audible was determined by ear and carefully checked by different operators. Further tests were made at high compression ratios to determine the power characteristics of the various fuels beyond the point of audible detonation. Indicator diagrams were obtained by means of a high speed indicator arranged to record a diagram representing the composite of several hundred explosions.

In making each test the engine was permitted to run long enough after all adjustments had been completed to permit conditions to become constant. The carburetor was adjusted to give maximum power output with each fuel tested when operating at a fixed compression ratio, and the adjustments so secured used with all tests which were made of that fuel. All the variable compression tests were made with the carburetor throttle held wide open, the load on the generator being varied until the engine speed was 1080 R. P. M. The temperature of the cooling water during all tests was maintained at 212 degrees F.

The following examples are given to illustrate the flexibility of the operation of the cracking apparatus illustrated and described. The most advantageous method of operation will, of course, depend on the market demand, as the apparatus may be operated to produce distillates representing different quantities of the oil charged and having widely different physical characteristics. Of the following examples the runs designated as Examples 1 and 2 were carried out in an apparatus substantially similar to the installation above described, in which a coil approximately 350 feet in length was employed as the digesting coil, whereas in the other runs a much longer coil was substituted therefor. The coil used in the latter tests was approximately 2300 feet in length, and a comparison of two runs made with the different equipment, but with substantially the same temperatures, pressures and rate of throughput will clearly illustrate the effect of the length of time of exposure to high temperatures on the quantity and character of the distillates obtained.

In each of the following runs steam was supplied from the boiler and superheater A at a temperature of about 1150 to 1200 degrees F. and fresh oil supplied to the system at a rate of about 180 gallons per hour.

The fresh oil charged was a 38 degree Bé. gas oil fraction from a Pennsylvania type crude oil. The boiler was operated so as to supply steam at a pressure of about 250 pounds per square inch and the steam receiver 39 maintained at a pressure of 225 pounds per square inch more or less as required to maintain the necessary flow of steam through the drums 10 to 1. The vapors in the digesting chamber 21 were maintained under a pressure of about 225 pounds, under which conditions a pressure of about 400 to 450 pounds per square inch was required at the pump 36 to maintain a flow of 180 gallons per hour of fresh oil through the heating coils. An appreciable drop in temperature of the steam between the heater A and the drum 10 was noted, and after substantially constant operating conditions were obtained the average temperature of the steam in the drum 10 was held at about 15 to 30 degrees F. higher than the average temperature of the oil vapors in the heating coil 20.

Example No. 1

Steam was circulated through drums 10 etc. at a rate regulated to maintain the temperature

of the oil vapors discharged from the coil 20 at approximately 975 degrees F. The vapors discharged from the digesting chamber 21 were condensed to form a single crude distillate product, which represented approximately 80% of the total oil charged, and had a gravity of 45 degrees Bé. Approximately 70% of the crude distillate was obtained as an overhead distillate by subsequent redistillation. The redistilled product had an end boiling point slightly below 437 degrees F., a gravity of 56 degrees Bé. and contained slightly in excess of 20% aromatic hydrocarbons. When tested as a motor fuel the redistilled product exhibited anti-detonating characteristics greatly superior to a blend comprising 50% benzol and 50% straight run Pennsylvania gasoline. About 4% on the fresh oil charged to the system was recoverable from the uncondensed vapors as a light distillate.

Example No. 2

Steam was circulated through drums 10 etc. at a rate sufficient to maintain the temperature of the oil vapors discharged from coil 20 at approximately 1020 degrees F. The vapors discharged from the digesting chamber 21 were condensed to form a single crude distillate product, which represented approximately 75% of the total oil charged. The crude distillate had a gravity of about 37 degrees Bé. On subsequent redistillation approximately 60% of the crude distillate was obtained as a 52 degree Bé.—overhead distillate having an end point slightly below 437 degrees F. About 6%, on the fresh oil charged to the system, was recoverable from the uncondensed gases as a light distillate. The redistilled product on analysis was found to contain 52.4% aromatic hydrocarbons and 24.8% other unsaturated hydrocarbons. Blends of the redistilled product with equal parts of straight run Pennsylvania gasoline when tested as a motor fuel in an internal combustion engine were found to have anti-detonating characteristics substantially the same as a blend composed of 50% pure benzol and 50% straight run Pennsylvania gasoline.

Example No. 3

This run was made using a digesting coil approximately six times as long as the digesting coil employed in the runs described in Examples 1 and 2. Steam was circulated through drums 10 etc. at a rate sufficient to maintain the temperature of the oil vapors discharged from the coil 20 at approximately 1050 degrees F. The vapors discharged from the digesting chamber 21 were condensed to form a single crude distillate product having a gravity of about 16.5 degrees Bé., which represented approximately 65% of the total oil charged. On subsequent redistillation 50% of the crude distillate was obtained as an overhead distillate having a gravity of 32.8 degrees Bé. and an end boiling point of approximately 437 degrees F. About 12% on the fresh oil charged through the system, was recoverable from the uncondensed gases as a light distillate. The redistilled product on analysis was found to contain 82.9% aromatic hydrocarbons, 17.1% other unsaturated hydrocarbons and no naphthene or paraffine hydrocarbons. A blend composed of 40% of the above distillate and 60% straight run Pennsylvania gasoline was found to have anti-detonating characteristics greatly superior to all blends of pure benzol and straight run Pennsylvania gasoline regardless of the benzol

content of the blend when tested as a motor fuel in an internal combustion engine. The 32.8 degree Bé. distillate when tested alone as a motor fuel was found to operate satisfactorily at all compression ratios below 11.2 to 1 without audible detonation under conditions, other than compression ratio, at which a straight run Pennsylvania gasoline would not operate without audible detonation when the compression ratio was increased to more than 4.3 to 1. Further, a blend of 50% of the 32.8 degree distillate with 50% straight run Pennsylvania gasoline was found to operate without audible detonation at a compression ratio of 6.45 to 1 under conditions other than compression ratio at which the straight run Pennsylvania would not operate without audible detonation when the compression ratio was increased to in excess of 4.3 to 1 and at which a blend composed of 50% pure benzol and 50% straight run Pennsylvania gasoline would not operate without audible detonation when the compression ratio was increased to 5.43 to 1. It will be apparent that the increment of increase in permissible compression ratio due to the addition to the straight run Pennsylvania gasoline of an equal volume of the 32.8 degree Bé. distillate product is approximately 100% in excess of the increment of increase due to the addition of an equal volume of pure benzol.

From the results obtained in a series of tests using blends of various percentages of the 32.8 degree distillate with straight run Pennsylvania gasoline and another series of similar tests using blends of the same percentages of pure benzol with straight run Pennsylvania gasoline, it was observed that as the percentage of pure benzol was increased the compression ratio at which detonation was first audible initially increased, but at a decreasing rate, reached a maximum when a blend containing approximately 50% benzol was used, and had decreased materially before the benzol content of the blends reached 70%, while, as the percentage of the 32.8 degree Bé. distillate was increased the compression ratio at which detonation was first audible increased at a consistently increasing rate which became very marked when the percentage of the distillate in the blend exceeded 30%.

A similar series of tests was made on a commercial gasoline which had anti-detonating characteristics slightly superior to those of the straight run Pennsylvania gasoline and on blends of the above distillate and of pure benzol with the commercial gasoline, using the same product for blending in both cases. In these tests it was noted that the ratio of the increment by which the compression ratio could be increased without audible detonation by the addition of a given percentage of the above distillate to the commercial gasoline relative to the increment by which the compression ratio could be increased without audible detonation by the addition of a similar percentage of pure benzol to the commercial gasoline was appreciably greater than the corresponding ratio of the increments by which the compression ratio could be increased without audible detonation by the addition of the same percentage of this distillate and of pure benzol respectively to samples of the straight run Pennsylvania gasoline. This was particularly noticeable with respect to the blends of lower benzol content.

It was also observed in making the above tests that when running the engine under full load over a prolonged period of time at the compression

sion ratio just below the point at which detonation would occur, the engine ran appreciably cooler as indicated by the temperature of the lubricating oil in the crank case when using blends of the above distillate as the motor fuel than when using corresponding blends of pure benzol as the motor fuel.

A 100 cc. sample of this 32.8 degree Bé. distillate when evaporated in a copper dish was found to leave about 60 mgs. of gum.

Example No. 4

A run was made using the same digesting coil 20 as employed in the run described in Example No. 3, but maintaining the temperature of the oil vapors discharged from the coil 20 at about 980 degrees F. The vapors discharged from the digesting chamber 21 were condensed as a single crude distillate product, having a gravity of 25 degrees Bé., representing about 70% of the total oil charged. About 8% of the oil charged was recoverable from the uncondensed gases as a light distillate. The effect of the time of exposure to the high temperature maintained in the digesting coil due to the greater length of the coil will be evident from a comparison of the gravity of the product and the yield obtained in this example as compared with those obtained in the run given as Example No. 1, during which substantially the same temperatures were maintained although a much shorter digesting coil 20 was employed.

Example No. 5

Another run was made using the same apparatus as employed in the runs given as Examples Nos. 3 and 4. During this run steam was circulated through the drums 10 etc. at a rate sufficient to maintain the temperature of the oil vapors discharged from the coil 20 at a temperature of 1030 to 1040 degrees F. The vapors discharged from the digesting chamber 21 were condensed as a single crude distillate product, having a gravity of 22 degrees Bé., representing about 68.5% of the total oil charged. An analysis of the crude distillate showed it to contain 96% unsaturated and aromatic hydrocarbon compounds. On subsequent redistillation approximately 53% of the crude distillate product was obtained as an overhead distillate having a gravity of 37.5 degrees Bé. and an end boiling point slightly below 437 degrees F. In addition, about 10% on the total oil charged was recoverable from the uncondensed gases as a light distillate.

A further portion of the crude distillate obtained from the run given as Example No. 5 was fractionally distilled, the cuts being made to give fractions having gravities as follows:

Degrees Bé.	Specific gravity
39.7	.826
22.6	.912
16.5	.956
13.6	.975
12.2	.985
11.3	.991
10.1	.999
2.28	1.016
5.04	1.036
7.95	1.058

gree Bé. fraction showed it to contain 23.8% unsaturated hydrocarbons and 72.2% aromatic hydrocarbons. It was impossible to obtain a complete analysis of the heavier fractions by the method of procedure above outlined due to solidification on nitration. Determination of the content of aromatic hydrocarbons in the heavier fractions was not possible by any known method of analysis. In order to determine the anti-detonating characteristics of the various components of the crude distillate product, runs were made in the test engine above described using blends of the various fractions with the straight run Pennsylvania gasoline as motor fuels. Separate runs were thus made using blends composed of 20% of the first four fractions listed above with 80% of the straight run Pennsylvania gasoline and in each case it was found possible to operate without audible detonation at a substantially higher compression ratio than that at which detonation became audible when using a blend of 20% pure benzol and 80% of the straight run gasoline as the motor fuel. Another similar test was made with a blend composed of 15% of the 10 degree Bé. gravity fraction with 85% of the straight run gasoline and in this case it also was found possible to operate without audible detonation at a compression ratio higher than that at which detonation became audible when using the 20/80% benzol blend.

A number of these intermediate and heavier fractions were found to have properties which make them of especial value as paint thinners. For example, a number of fractions having gravities ranging from 13 to 34 degrees Bé. when used as paint thinners were found to give good distribution and although they had relatively high flash and boiling points, dried readily and without discoloration. The heavier distillates were also found to have an exceptionally low viscosity and exceptionally low cold test as compared to ordinary petroleum distillates of the same gravity. For example, the 22.6 degree Bé. fraction was found to have a net viscosity of 300 at 60 degrees F. as measured by a standard thermo-viscosimeter, the 11.3 degree Bé. fraction to have a net viscosity of 650 at 80 degrees F. as indicated by the thermo-viscosimeter or 54 seconds Saybolt at 80 degrees F., while the heaviest of the above fractions, having a specific gravity of 1.058, was found to have a viscosity of 184 seconds Saybolt at 80 degrees F. and to solidify at minus 30 degrees F.

The freezing points of the 39.7 degree Bé. fraction and of the 32.8 degree Bé. distillate, obtained by redistillation of the crude distillate products from the runs given as Examples 5 and 3 respectively as above described, were found to be below minus 40 degrees F., notwithstanding the large percentage of aromatic hydrocarbons contained in these distillates. The actual freezing point of these distillates was not determined because minus 40 degrees F. was the lowest temperature which could be obtained with the testing equipment used, although at this temperature both of these distillates were perfectly fluid and would not solidify even on the addition of benzol seed crystals.

Having thus described my invention, what is claimed as new is:

1. The process of manufacturing a high anti-knock motor fuel product containing in excess of 50% aromatic hydrocarbons boiling within the gasoline range, which comprises passing a hydrocarbon oil distillate which is substantially free of

Analysis of the 39.7 degree Bé. fraction which included all of the lighter constituents contained in the crude distillate product showed it to contain 25.6% unsaturated hydrocarbons, 63.4% aromatic hydrocarbons and 11.0% naphthene and paraffine hydrocarbons. Analysis of the 22.6 de-

hydrocarbons boiling in the range of said product in a confined stream of restricted cross section through a long heating coil, maintaining a pressure on the outlet of said coil of approximately 225 pounds per square inch or higher, heating the oil in the initial part of said coil to vaporize the same and raise the temperature thereof to approximately 900° F. to 1000° F., continuing the heating of the vaporized oil products in the latter portion of said coil under digesting conditions for a considerable period of time at a controlled temperature during which heat is supplied to the vapors at substantially the rate at which heat is absorbed in the reactions taking place, discharging the highly heated products from said coil at a temperature between about 975° F. and 1050° F. and passing them into an enlarged heat insulated reaction zone to which no heat is supplied from an external source and the vapors are maintained above their cracking temperature by their self-contained heat, maintaining the oil constituents in the digestion portion of said coil and said enlarged zone for a period of time sufficient to secure a conversion per pass of at least 40% of constituents boiling below approximately 437° F. and which contains in excess of 50% of aromatic hydrocarbons, and thereafter recovering the constituents suitable as motor fuel from products resulting from the cracking operation.

2. The process of making a high anti-knock motor fuel having a boiling point curve of the type of that of straight run gasoline and comprising in excess of 50% aromatic hydrocarbons, which comprises cracking a higher boiling non-aromatic hydrocarbon oil distillate which is substantially free of gasoline constituents by passing it in a stream of restricted cross-section through an elongated heated passage maintained under an outlet pressure of at least 225 lbs. per square inch, heating the same to a selected cracking temperature between 900° and 1000° F. in the first portion of said passage, continuing the heating of the oil constituents in vapor phase in the remaining portion of said passage at or slightly above said selected temperature and within the range of from approximately 975° F. to 1050° F. at which temperature the cracked products are discharged from said heated passage, and maintaining the oil constituents at about said selected temperature for a period of time in excess of that necessary to effect a 40% conversion of the oil into constituents suitable as gasoline while passing once through said passage, thereby converting a substantial proportion of the oil into said high anti-knock motor fuel.

3. The process of manufacturing a high anti-knock gasoline motor fuel product containing in excess of fifty per cent aromatic hydrocarbons, which comprises heating a hydrocarbon gas oil distillate which is substantially free of constituents boiling within the range of said gasoline product while passing the same in a confined stream of restricted cross section through a heating zone to raise the temperature of the distillate to and maintain it at a selected cracking temperature between 975° and 1050° F., maintaining the said distillate under a pressure of at least 225 lbs. per square inch and at approximately the temperature reached in said heating for a period of time substantially in excess of that required at said temperature to convert the constituents of said distillate into a maximum possible yield of constituents suitable as motor fuel without excessive production of carbon and fixed gas, said period of time also being sufficient to convert said

distillate and to produce a motor fuel fraction of approximately 437° F. end point containing from fifty to eighty per cent aromatic hydrocarbons, said period of time being such as to permit a recovery of at least 40% of motor fuel having an end point of approximately 437° F. from the cracked products discharged from the cracking operation, and thereafter recovering the constituents suitable as motor fuel from the products resulting from the heating of said distillate.

4. The method of producing a low boiling motor fuel product having anti-knock characteristics which comprises, flowing a higher boiling substantially completely vaporizable distillate oil which is substantially free of constituents boiling within the range of said product through a coil, maintaining a pressure on the outlet thereof of about 225 lbs. per square inch or higher, heating the said oil in its flow through said coil from substantially below a cracking temperature to a cracking temperature, completely vaporizing the oil and bringing the resulting vapors to a cracking temperature above 900° F. but not substantially above 975° F. in a portion of said coil, passing the heated vapors into an enlarged chamber and causing them to travel slowly there-through while maintaining thereon a pressure approximating the outlet pressure on the coil and a temperature above 850° F. but not substantially above 975° F., and retaining the vapors in the coil and the enlarged chamber at said cracking temperature and without condensing any portion thereof for a sufficient period of time to secure a conversion thereof into motor fuel products in the gasoline boiling point range in a minimum amount per pass of at least 13%, the heating of the oil in said coil being accomplished at such a rate that the major part of the cracking is effected after the oil has been completely vaporized, whereby a motor fuel product in the gasoline boiling point range having a high anti-knock value is secured.

5. The method of producing a low boiling motor fuel product having relatively high antiknock characteristics, which comprises passing a higher boiling substantially completely vaporizable hydrocarbon oil which is substantially free of constituents boiling within the range of said product once only through a heating coil while maintaining at the outlet thereof a pressure of about 225 lbs. per square inch or higher, heating the oil in its flow through the initial portion of said coil to vaporize the oil and raise it to a temperature above 900° F. and not substantially above 975° F., maintaining the vapors in the remaining portion of said coil for a substantial period of time at said cracking temperature above 900° F. and not substantially above 975° F. to secure a total cracked product in the gasoline range of boiling points in a minimum amount of at least 13% of the total material treated per pass through said coil, said conversion operation being so controlled that a major part of the cracking is effected after the oil has been vaporized, whereby a product having relatively high anti-knock properties has been produced.

6. The process of producing a low boiling anti-knock gasoline motor fuel product, which comprises passing a distillate oil which is substantially free of gasoline constituents in a stream of restricted cross section through a heating zone and heating the oil therein to a temperature in excess of 900° F., conducting all of the resulting heated oil constituents into and through a second heating zone in a stream of restricted cross sec-

tion and therein subjecting the oil constituents to digestion at a temperature of from about 975° to 1050° F., discharging the cracked and converted oil from said second zone, subjecting the oil to cracking conditions for a prolonged period of time sufficient to secure 40% conversion of the oil to gasoline per pass, said period including maintaining the heated oil constituents in the digestion zone for a period of time approximating that required for a gas-oil at a temperature of 900° F. and a pressure of 225 lbs. per square inch to pass through a coil one inch in diameter and 2300 feet long when the oil is introduced into said coil at a rate corresponding to 180 gallons of liquid oil per hour, maintaining a substantial superatmospheric pressure in said zones, and fractionating the said converted oil discharged from said second zone to separate out a gasoline motor fuel.

7. The process of producing a low boiling high antiknock gasoline motor fuel product by the cracking of oil charging stocks such as gas-oil, paraffin base distillate and heavy naphtha, which comprises passing such a cracking stock at a relatively high superatmospheric pressure and at a high velocity through a long heating coil in a confined stream of restricted cross section, heating the oil in its passage through the initial part of said coil to vaporize the oil stock and raise it to a cracking temperature but not in excess of

about 900° to 1000° F., continuing the heating of the vaporized oil products in the vapor phase under digesting conditions in the remaining portion of said coil but without raising the temperature thereof in excess of about 1050° F. said heating and digesting of the oil constituents in said remainder of said coil being continued for a period of time approximating that required for a gas-oil at a temperature of 900° F. to pass through a coil one inch in diameter and approximately 2300 feet long at a discharge pressure of about 225 pounds per square inch when the said gas-oil is supplied thereto at a rate corresponding to 180 gallons of liquid gas-oil per hour, discharging the highly heated and cracked products from the outlet of the digestion portion of said coil under a pressure of approximately 225 pounds per square inch or higher, and fractionating the resulting conversion products of the cracking reaction to separate out said high anti-knock gasoline motor fuel product.

8. The process defined by claim 7 in which the highly heated products discharged from the digestion portion of said coil are further digested in an enlarged heat insulated zone during which no heat is supplied from an external source and the vapors are maintained above their cracking temperature by their self-contained heat.

CHAUNCEY B. FORWARD.